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SQUARE WAVE VOLTAMMETRY AT THE DROPPING MERCURY ELECTRODE: EXPE--ETC(U)

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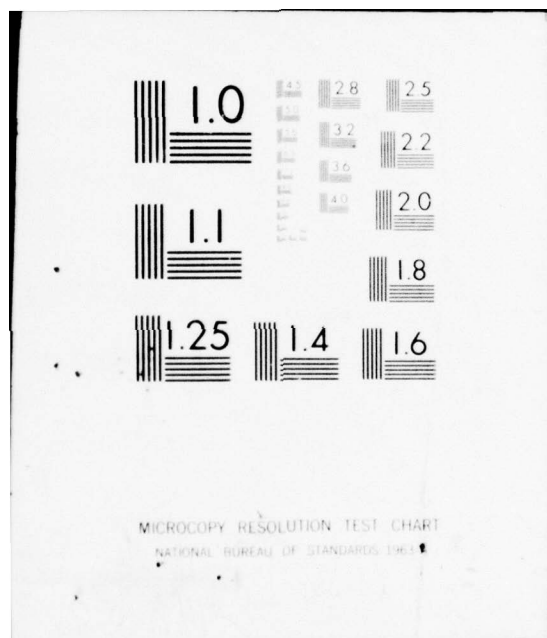
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SQUARE WAVE VOLTAMMETRY

AT THE DROPPING MERCURY

ELECTRODE: EXPERIMENTAL

by

John A. Turner, J. H. Christie, M. Vukovic and R. A. Osteryoung

Colorado State University  
Department of Chemistry  
Fort Collins, Colorado 80523

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## BRIEF

Experimental aspects of square wave voltammetry at the dme are discussed. The technique has the same order of sensitivity as differential pulse polarography but is much faster to perform.

## ABSTRACT

Experimental verification of earlier theoretical work for square wave voltammetry at the dropping mercury electrode is given. Experiments using ferric oxalate and cadmium (II) in HCl confirm excellent agreement with theory. Experimental peak heights and peak widths are found to be within 2% of calculated results. An example of trace analysis using square wave voltammetry at the dme is presented. The technique is shown to have the same order of sensitivity as differential pulse polarography but is much faster to perform. A detection limit for cadmium in 0.1 M HCl for the system used here was  $7 \times 10^{-8}$  M.

*10% the minus 8th power*

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## SQUARE WAVE VOLTAMMETRY AT THE DROPPING MERCURY ELECTRODE: EXPERIMENTAL

One of the few disadvantages of pulse polarography is that the time required for the scan of a potential range is often rather long. Particularly at trace concentrations of analyte, long drop times are required to maximize the ratio of faradaic to capacitative current (1); long drop times require correspondingly slow sweep rates to obtain the desired resolution.

Stationary electrodes can be used to significantly decrease the time of analysis since higher scan rates can typically be employed. However, the advantages of the dme's renewable surface are lost at a stationary electrode.

The other alternative is to apply the entire potential scan to a single drop of a dme as is done in "cathode-ray polarography." However, the high background currents generated by the rapid dc ramp severely limits the usefulness of this technique. The charging current generated by the high speed linear ramp is so great that combining a square wave wave form with it for use at a dme results in only limited success (2,3).

Blutstein and Bond (4) have presented a technique for scanning the entire potential range in a single drop, and have termed it "fast sweep differential pulse polarography." Again, a sweep linear ramp is used as the base potential sweeping function and the technique is limited by the charging current background that the ramp generates.

Barker (5) in 1957 reported the application of square wave to a single drop of a dme. More recently he has published a preliminary note (6) concerning a multimode polarograph that is capable of scanning limited voltage ranges during the life of a drop.

Ramaley and Krause (7,8) combined a staircase wave form with a square wave and called it square wave voltammetry. The theory they developed (7) was basically a modification of Barker's original treatment of square wave

polarography (9,10) and required normalization to compensate for the distortion introduced by the staircase. They presented some experimental results at a hanging mercury drop for the technique (8), but they did not apply it to a dme.

Since a staircase is used as the base potential sweeping function, the technique should show a high degree of discrimination against double layer charging, even at the high sweep rates needed for use at a single drop of a dme. In their technique of applying the wave form, the staircase step was subtracted from the reverse pulse of the square wave. In increasing the step height to increase the sweep rate, the reverse pulse would be smaller by an amount equal to the step height, with a corresponding loss in sensitivity. If, on the other hand, the staircase were added to the forward pulse, there would be no loss in sensitivity as the step height was increased. This possibility was discussed by Ramaley and Krause (7) but apparently never implemented.

We have recently (11) presented a theoretical treatment for the case where the step height is added to the forward going square wave pulse. The treatment is slightly more elegant in that the affect of the staircase is explicitly included and new variables and associated nomenclature have been introduced.

This paper concerns itself with the experimental verification of our earlier theoretical work and the application of square wave voltammetry at the dme to trace analysis.

## EXPERIMENTAL

Since the wave form is entirely digital, it becomes reasonable to apply the wave form with a computer via a digital to analog (D/A) converter. The computer can also acquire the current values and display the results. Because the entire scan is completed in a single drop, it is also possible to do a large number of ensemble averages with a computer for low level trace work.

A PDP-12 computer (Digital Equipment Corporation) was used for on-line experiments and analysis of data. The system as presently configured consists of 24k of magnetic core, scope, x-y plotter, two 12-bit D/As, one 12-bit A/D, dual magnetic tape, disk and floating point processor. The interface and associated hardware have been previously described (12). Two computer programs were utilized in this work, one written in Real Time FORTRAN IV runs under DEC's system OS/8, while the other is an assembly language program that runs under DIAL. The data acquired using the FORTRAN program was analyzed off-line using another FORTRAN program. The data from the assembly language program was analyzed off-line using FOCAL language.

Either a PAR model 174 or 173 (Princeton Applied Research) was used as a potentiostat and I-E converter, the PAR 173 is equipped with a Model 179 Digital Coulometer. The dropping mercury electrode assembly was the PAR Model 9337 polarography stand with a PAR Model 172A drop knocker driven by the computer. The cell was a 100 ml berzelius beaker. A saturated calomel electrode from Sargent Welch (30080-15A) with a porous platinum tip was used as reference. The counter electrode was a platinum helix separated from the solution by a pyrex tube with a pinhole in the bottom. Triple distilled mercury (Bethlehem Apparatus Co.) was used. Deaeration was done with prepurified nitrogen further purified by passage over hot copper wool.

The oxalate solution was a 0.5M potassium oxalate and 0.5M oxalic acid buffer made by mixing appropriate amounts of Baker reagent grade potassium carbonate and oxalic acid, pH = 4. A concentrated standard iron solution was made by dissolving Baker reagent grade iron wire in hot dilute hydrochloric acid. The iron oxalate solution was made fresh daily as recommended by Lingane (13). The concentration of iron(III) oxalate used was  $5.056 \times$



$10^{-4}$  M. For the cadmium experiments, an  $8.43 \times 10^{-5}$  M cadmium solution in 0.1M HCl was used, made up by diluting previously standardized concentrated cadmium stock. Capillary flow rates were measured at the end of each set of experiments at open circuit in the experimental solution. The values were as noted.

IR compensation was not used for any data presented here.

Diffusion coefficients were measured using normal pulse polarography in the same experimental solution as the data was taken. From iron, the result was  $6.2 \times 10^{-6} \text{ cm}^2/\text{sec}$  at  $25^\circ\text{C}$  using a drop time of 3 sec., pulse width of 50 msec, and a flow rate of .93 mg/sec. This is in excellent agreement with Lingane's value of  $6.1 \times 10^{-6} \text{ cm}^2/\text{sec}$  at  $25^\circ\text{C}$  (calculated from the diffusion current constant =  $1.50 = 607 n D^{1/2}$ ) (13) but only fair agreement with the number reported by Smith (14) of  $4.94 \times 10^{-6}$  from ac data. For cadmium, the result was  $8.11 \times 10^{-6} \text{ cm}^2/\text{sec}$  at  $20^\circ\text{C}$ , 3 sec. drop time, 50 msec pulse width and a flow rate of .719 mg/sec. This is in good agreement with the number of  $7.91 \times 10^{-6} \text{ cm}^2/\text{sec}$  given by Fonds et al (15) and by Osteryoung (16).

#### RESULTS AND DISCUSSION

The theoretical dependence of the square wave difference current is given by (11)

$$\Delta I_j^+ = \frac{n F A D_0^{1/2} C^*}{\sqrt{\pi \tau}} \Delta \psi_j^+ (E_{sw}, \Delta E, \rho_1, \rho_2, \sigma)$$

where  $\tau$  is the step time (frequency $^{-1}$ ) and  $\Delta \psi_j^+$  is the normalized square wave current function, dependent on the square wave amplitude ( $E_{sw}$ ), the step height ( $\Delta E$ ), the time of measurement of the individual forward and reverse currents ( $\rho_1 \tau$ ,  $\rho_2 \tau$  respectively) and the symmetry of the wave form (given by  $\sigma$ ).

Since the experiment involves scanning the entire potential range of interest at a single drop of a dropping mercury electrode, the area of the

electrode is constantly growing throughout the scan, at a rate proportional to the 2/3 power of time. Experimental currents are therefore normalized to the delay time (or any other time) by

$$i_{\text{normalized}} = i_{\text{measured}} \left( \frac{t}{t_D + J\tau} \right)^{2/3}$$

where

$t_D$  = the delay time

$t$  = time currents are being normalized to ( $=t_D$  for normalization to delay time)

$J$  = 1,2,3... = number of cycles to that point.

Figure 1 compares the calculated and observed peak height dependence on  $E_{\text{sw}}$  for the iron and cadmium systems. The agreement is excellent. Differences between the observed peak currents and calculated values average 1.1% for the iron system and less than 2% for the cadmium system.

Figure 2 shows the dependence of the peak half-widths on  $E_{\text{sw}}$ ; agreement for both is better than 1%.

Figure 3 shows the forward and reverse currents for two different square wave amplitudes for the iron system. Although not shown, the theoretical currents are virtually superimposable. The experiment confirmed the expected behavior from theory. At the low  $E_{\text{sw}}$ , the currents do have the same sign and subtraction results in a difference current less than the forward current alone. The higher  $E_{\text{sw}}$  results in currents that are opposite in sign and the difference current will be enhanced over the forward pulse current alone. The point that needs to be made is that in order to obtain maximum sensitivity for square wave, the reverse pulse must reverse the electrode reaction, not just reduce it. With that in mind, if one is having problems with system response, it is better to decrease the frequency than to decrease the amplitude.



Figure 4 shows a square wave polarogram for cadmium along with the individual forward and reverse currents. The individual currents as well as the difference current correspond very closely to theory, showing that even for an amalgam, the system is well behaved.

Table I reports the peak current data as a function of the  $2/3$  power of delay time for the cadmium system. The peak currents have been normalized to the delay time. The consistency of the ratio indicates the effectiveness of the area normalization. The agreement between theory and experiment is excellent. The low values for the .5 and 1.0 sec point indicate evidence of a depletion effect.

The peak current should be a linear function of the inverse square root of step time. Table II presents this data for the cadmium system. The agreement between theory and experiment is again excellent. The 50 and 66.7 msec points are probably showing some effect due to depletion while the ratio for the 10 and 8 msec points indicates incomplete decay of charging current.

Figure 5 shows the effect of the symmetry factor  $\sigma$  on the peak current for the iron system. As previously discussed (11), the minimum point is dependent on square wave amplitude and the step height but is usually between 0.4 and 0.6. One reason for the higher deviation of the experimental values at the ends is probably due to incomplete decay of charging current.

#### Anodic Scans

When scanning in the anodic direction the initial potential is set such that the diffusion limited current is maintained while the drop is growing. After the delay time, the scan proceeds in the anodic direction. For an amalgam system this is analogous to a stripping experiment, and indeed experiments have shown (17,18,19) that there is a definite enhancement of the anodic over the cathodic wave. However, calculations and

experiments using iron oxalate (18,19) indicate that there should be no difference between the two scans. What causes the enhancement is still under debate; there is some thought that it may have something to do with the flow patterns in the growing mercury drop.

Square wave also shows an enhancement in the wave when anodic scans are made. For example, a plot of peak current vs. the  $2/3$  power of delay time gives a slope of 1.83 in contrast to 1.40 for the cathodic scan. A plot of peak current vs. square wave amplitude (Figure 6) also shows a marked increase. It should be pointed out that the peak half-width are in excellent agreement with theory.

#### Depletion Effect

For the iron system where both species are solution soluble, no depletion effect was found. The results are identical whether scans are on successive drops or several drops are skipped in between. The reason for this is probably a combination of two effects: (1) since the potential is reset to the initial potential between scans, any of the reduced species remaining near the end of the capillary will be reoxidized during the delay time, and (2) the cyclic nature of the square wave. The cadmium system, on the other hand, forms an amalgam and the drop will carry that away as it falls. A first drop effect is therefore expected for this system.

As it turns out, the depletion effect for an amalgam system depends on the number of averages, delay time, and how long the drop sits completely polarized. If averages are done without skipping drops, the average current drops from the first drop value, leveling off after an average of 10 or so. This leveling off is probably due to each run depleting the solution a little bit more until a steady state is reached and the way an average asymptotically approaches the final value. Shorter delay times (1 sec.

or less) show larger depletion effects presumably from the drop having insufficient time to grow into a nondepleted area. The length of time the drop sits completely polarized depends on a combination of the scan rate, potential range scanned and the position of the peak with respect to the initial potential. The faster the scan rate, the smaller the depletion due to the shorter amount of time the drop sits completely polarized. If the potential range is large (a volt or so) a peak near the initial potential will be more affected than one near the end of the potential scan.

For the anodic scan, there is a reverse first drop effect. In an anodic scan, the initial potential is set such that cadmium ion is reduced and cadmium amalgam is formed as the drop grows. As the scan proceeds anodically, the cadmium in the drop is stripped out and the next drop will grow in a slightly enriched solution. The variables that affect the height of the peak are identical to the ones for the cathodic scan except the action of each on the current is exactly opposite.

Under most conditions, the effect is not large, less than two percent, and by judicious choice of system parameters, the affect due to depletion can be minimized. It can therefore usually be ignored. For this work, drops were not skipped between runs unless otherwise noted. As previously discussed, this will have no affect on the iron results; for the cadmium system, the affect is less than 2%. Places where depletion could be larger than that have been noted.

#### Trace Analysis

Figure 7 gives an example of the use of this technique at the trace level. The background is due to dc charging from drop growth (20) and has the same shape as a differential capacity curve. Total analysis time for the 30 drop average was 2.5 mins. It is obvious that there are going to be problems with measurement of copper at this level. The background for lead

and cadmium is much flatter and measurement of these will be easier. Table 3 gives data for a calibration curve for cadmium. The curve was made by doing standard additions using microliter pipettes. Peaks were measured by extrapolation of background on each side of the peak. The experimental slope is in excellent agreement with theoretical, showing that the system even at this level is well-behaved. A depletion effect is not expected for cadmium here because it is near the end of the potential scan. A depletion effect would be expected for copper; however, difficulty in measurement of the peak prevented the testing of this.

A detection limit was calculated by putting a least square line through the background from  $-0.5$  to  $-0.7$  volts and measuring the standard deviation. Defining the detection limit as (21)

$$C = 3 S/m$$

where  $S$  is the standard deviation of the blank and  $m$  is the slope of the analytical line. The detection limit for cadmium was  $7 \times 10^{-8}$  M. Using the method of Skogerboe and Grant (22) for three determinations at the  $1.3 \times 10^{-7}$  M level, the detection limit was again  $7 \times 10^{-8}$  M.

Anson (23) has recently shown that in the presence of anion induced adsorption, differential pulse polarography on the cation concerned results in an increased peak current. Similar results are found in square wave voltammetry at the dme. The results for cadmium in nitrate and iodide solution are shown in Figure 8. At low concentrations of  $\text{Cd(II)}$ , which is adsorbed in the iodide solutions, a significant fraction of the current results from the reaction of the adsorbed material; at higher  $\text{Cd(II)}$  concentrations, the fraction of the current arising from the adsorbed, vis-a-vis the diffusing source, diminishes. The implications for analytical work are obvious.



The use of the square wave voltammetric method at the dropping mercury electrode appears to have all the sensitivity of differential pulse polarography, with the advantage of much less time required for analysis. Clearly, the requirement of a digitally oriented system is a disadvantage, but the technique is obviously adaptable to microprocessor instrumentation.

An instrument capable of performing square wave voltammetry employing digital circuitry is under construction in our laboratory and will be reported on at a later date (24).

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## LITERATURE CITED

1. J. H. Christie and R. A. Osteryoung, *J. Electroanal. Chem.*, 49, 301 (1974).
2. Y. Saito and K. Okamoto, *Rev. Polarog. (Kyoto)*, 10, 227 (1962).
3. K. Okamoto, "Modern Aspects of Polarography," T. Kambara, Ed., Plenum Press, N. Y., 1965, p. 225.
4. H. Blutstein and A. M. Bond, *Anal. Chem.*, 48, 248 (1976).
5. G. C. Barker, *Congr. on Anal. Chem. in Ind.*, St. Andrews, June, 1957.
6. G. C. Barker, A. W. Gardner and M. J. Williams, *J. Electroanal. Chem.*, 42, App 21 (1973).
7. L. Ramaley and M. S. Krause Jr., *Anal. Chem.*, 41, 1362 (1969).
8. M. S. Krause, Jr. and L. Ramaley, *Anal. Chem.*, 41, 1365 (1969).
9. G. C. Barker, P. L. Faircloth and A. W. Gardner, *Atomic Energy Research Establ. (Gt. Brit.)*, C/R-1786.
10. G. C. Barker, *Anal. Chem. Acta*, 18, 118 (1958).
11. J. H. Christie, J. A. Turner and R. A. Osteryoung, *Anal. Chem.*, submitted for publication (1977).
12. J. H. Christie, Ph.D. Thesis, Colorado State University, April 1974.
13. J. J. Lingane, *J. Amer. Chem. Soc.*, 68, 2448 (1946).
14. D. E. Smith and W. H. Reinmuth, *Anal. Chem.*, 33, 482 (1961).
15. A. W. Fonds, A.A.A.M. Brickman, and J. M. Los, *J. Electroanal. Chem.*, 14, 43 (1962).
16. J. Osteryoung, private communication.
17. R. A. Osteryoung and E. P. Parry, *J. Electroanal. Chem.*, 9, 299 (1965).
18. J. H. Christie, L. L. Jackson and R. A. Osteryoung, *Anal. Chem.*, 48, 561 (1976).
19. L. L. Jackson, unpublished results.
20. J. H. Christie and R. A. Osteryoung, *J. Electroanal. Chem.*, 49, 301 (1974).
21. J. A. Turner, R. H. Abel and R. A. Osteryoung, *Anal. Chem.*, 47, 1343 (1975).

22. R. K. Skogerboe and C. L. Grant, Spectrosc. Lett., 3, 215 (1970).
23. F. C. Anson, J. B. Flanagan, K. Takahashi and Y. Yamade, J. Electroanal. Chem., 67, 253 (1976).
24. C. Yarnitzky and R. A. Osteryoung, unpublished results.

TABLE I

Peak current dependence on the 2/3 power of the delay time for the cadmium system.

$t_d$	$t_d^{2/3}$	Normalized Peak Current	Ratio $i_p/t_d^{2/3}$
(sec)	(sec) <sup>2/3</sup>	( $\mu$ A)	
.5	.630	.864	1.37
1.0	1.00	1.38	1.38
2.0	1.59	2.22	1.40
3.0	2.08	2.91	1.40
4.0	2.52	3.54	1.40
5.0	2.92	4.12	1.41

Theoretical Ratio = 1.40

Conditions:  $\Delta E = 5$  mV,  $E_{sw} = 30$  mV,  $\sigma = 0.5$ ,  $\rho_1 = 0.499$ ,  $\rho_2 = 0.999$ ,  
 $m = .719$  mg/sec.

Currents normalized to delay time.

TABLE II

Peak current dependence on inverse square root of step time for the cadmium system.

$\tau$ (msec)	$\tau^{-1/2}$ (sec) <sup>-1/2</sup>	Normalized Peak Current	Ratio $i_p/\tau^{-1/2}$
66.7	3.87	1.55	.401
50.0	4.47	1.76	.394
40.0	5.0	2.03	.406
33.3	5.48	2.21	.403
30.0	5.77	2.34	.405
25.0	6.32	2.57	.407
16.7	7.74	3.14	.406
10.0	10.00	4.11	.411
8.0	11.18	4.70	.420

Theoretical Ratio = .407

Conditions:  $\Delta E = 5$  mV,  $E_{sw} = 30$  mV,  $\sigma = 0.5$ ,  $\rho_1 = 0.499$ ,  $\rho_2 = 0.999$ ,  
 $m = .719$  mg/sec, normalization time = 2 sec.



TABLE III

Calibration Curve for Cadmium in 0.1 M HCl

Conc. M x 10 <sup>7</sup>	nA	ip/C*
.84	8.0	7.7
1.26	10.7	7.3
2.11	18.0	7.8
4.22	30.0	6.8
6.32	47.0	7.2
8.42	64.0	7.4

Slope =  $7.3 \pm .2$ 

Theoretical Slope = 7.27

Intercept =  $1.5 \pm 1.0$ 

Standard Error of line = 1.4

Conditions same as Figure 7

Currents not normalized

\*Currents for ratio corrected for  
nonzero intercept.



## FIGURE CAPTIONS

FIGURE 1 Dependence of peak current on square wave amplitude.

Points experimental - line theoretical

(●) Iron System

$$\tau = 33.3 \text{ msec}$$

$$\sigma = 0.5$$

$$\rho_1 = .499$$

$$\rho_2 = .999$$

$$\Delta E = 5 \text{ mV}$$

$$t_d = 2 \text{ sec}$$

$$m = .93 \text{ mg/sec}$$

$$\text{ave} = 10$$

Instrument PAR 174

(◆) Cadmium System

$$\tau = 33.3 \text{ msec}$$

$$\sigma = 0.5$$

$$\rho_1 = .499$$

$$\rho_2 = .999$$

$$\Delta E = 5 \text{ mV}$$

$$t_d = 2 \text{ sec}$$

$$m = .72 \text{ mg/sec}$$

$$\text{ave} = 10$$

Instrument PAR 173

Currents normalized to the delay time

FIGURE 2 Dependence of peak width at half-height on  $E_{sw}$ . Conditions and legend same as Figure 1.

FIGURE 3 Experimental currents for the iron oxalate system.  $\tau = 33.3 \text{ msec}$ ,

$\sigma = 0.5$ ,  $\rho_1 = .499$ ,  $\rho_2 = .999$ ,  $\Delta E = 5$  mV,  $t_d = 2$  sec,  $m = .93$  mg/sec, Ave - 10.

(A)  $E_{sw} = 5$  mV

(B)  $E_{sw} = 30$  mV

Currents normalized to the delay time. Instrument PAR 174.

FIGURE 4

Experimental currents for the cadmium system.  $\tau = 33.3$ ,

$\sigma = 0.5$ ,  $\rho_1 = 0.499$ ,  $\rho_2 = .999$ ,  $\Delta E = 5$  mV,  $E_{sw} = 30$  mV,

$t_d = 2$  sec,  $m = .719$  mg/sec, Ave = 10.

(A) Difference current

(B) Forward and reverse currents

Points experimental - line theoretical. Currents normalized to the delay time. Instrument PAR 173.

FIGURE 5

Variation of  $I_p$  on  $\sigma$ . Iron oxalate system used. Points experimental - line theoretical.

$\tau = 33.3$

$\rho_1 = \sigma - 0.05$

$\rho_2 = .995$

$\Delta E = 5$  mV

$E_{sw} = 20$  mV

$t_d = 5$  sec

$m = .933$  mg/sec

ave = 30

Instrument PAR 173. Currents normalized to delay time.

FIGURE 6

Dependence of peak current on square wave amplitude, anodic scan - cadmium system. Points experimental - line theoretical. Conditions same as Figure 1.

FIGURE 7

Example of trace analysis using square wave voltammetry at the dme. Supporting electrolyte is 0.1 M HCl.

$$\tau = 16.7$$

$$\sigma = 0.5$$

$$\rho_1 = 0.499$$

$$\rho_2 = .999$$

$$\Delta E = 5 \text{ mV}$$

$$E_{sw} = 30 \text{ mV}$$

$$m = .995 \text{ mg/sec}$$

$$t_d = 2 \text{ sec}$$

$$\text{ave} = 30.$$

Instrument PAR 173. Currents normalized to delay time.

Concentrations  $\text{Cu} = 2.3 \times 10^{-7} \text{ M}$  (15 ppb)

$\text{Pb} = 2.4 \times 10^{-7} \text{ M}$  (50 ppb)

$\text{Cd} = 2.1 \times 10^{-7} \text{ M}$  (24 ppb)

FIGURE 8

Normalized peak height for cadmium in 0.2 M  $\text{KNO}_3$  (◆), pH = 3; 0.1 M KI (●).  $\Delta E = 5 \text{ mV}$ ,  $E_{sw} = 40 \text{ mV}$ , delay time = 2 sec,  $\tau = 30 \text{ msec}$ ,  $\sigma = 0.5$ ,  $\rho_1 = .48$ ,  $\rho_2 = .96$ , Ave = 10.

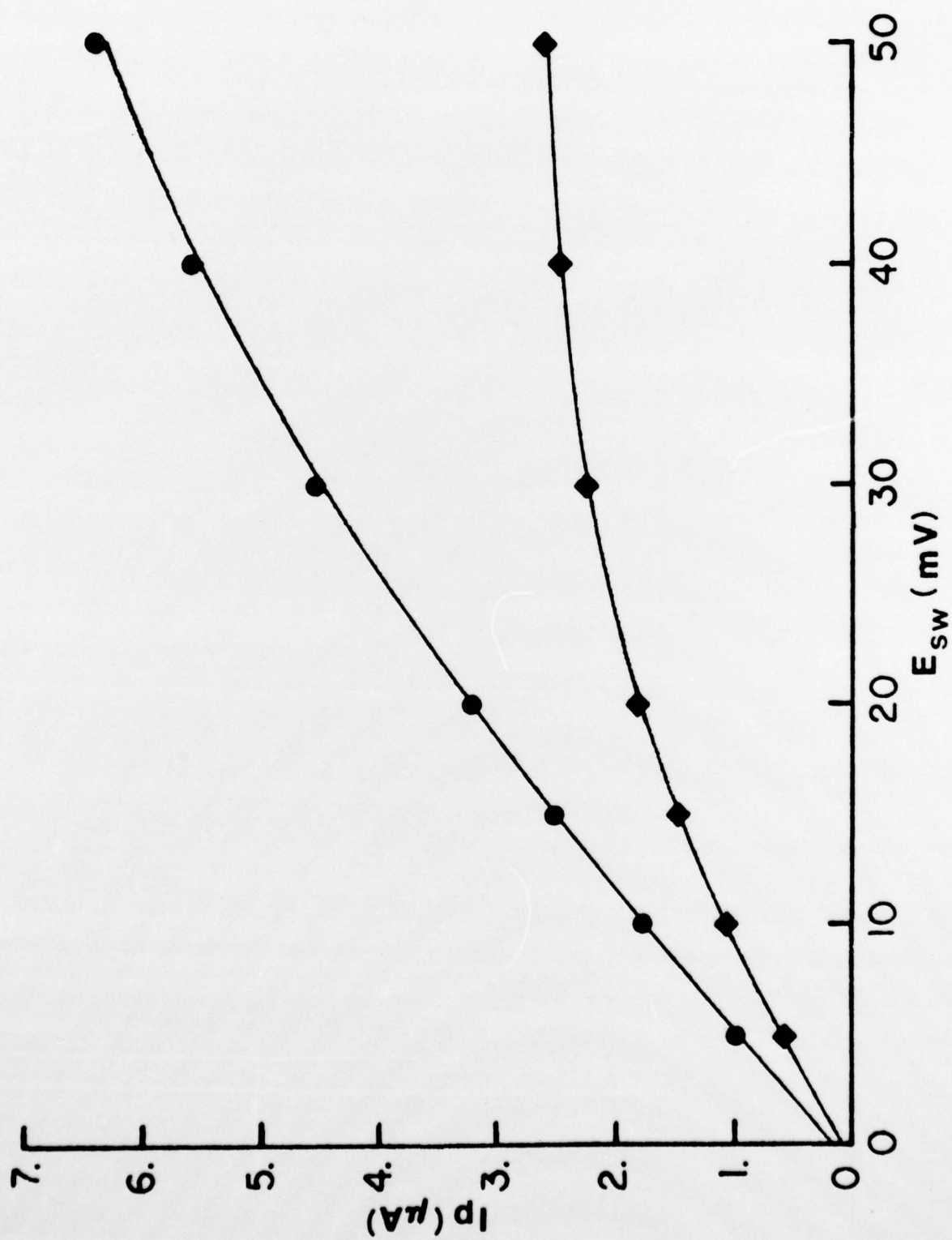


FIGURE 1

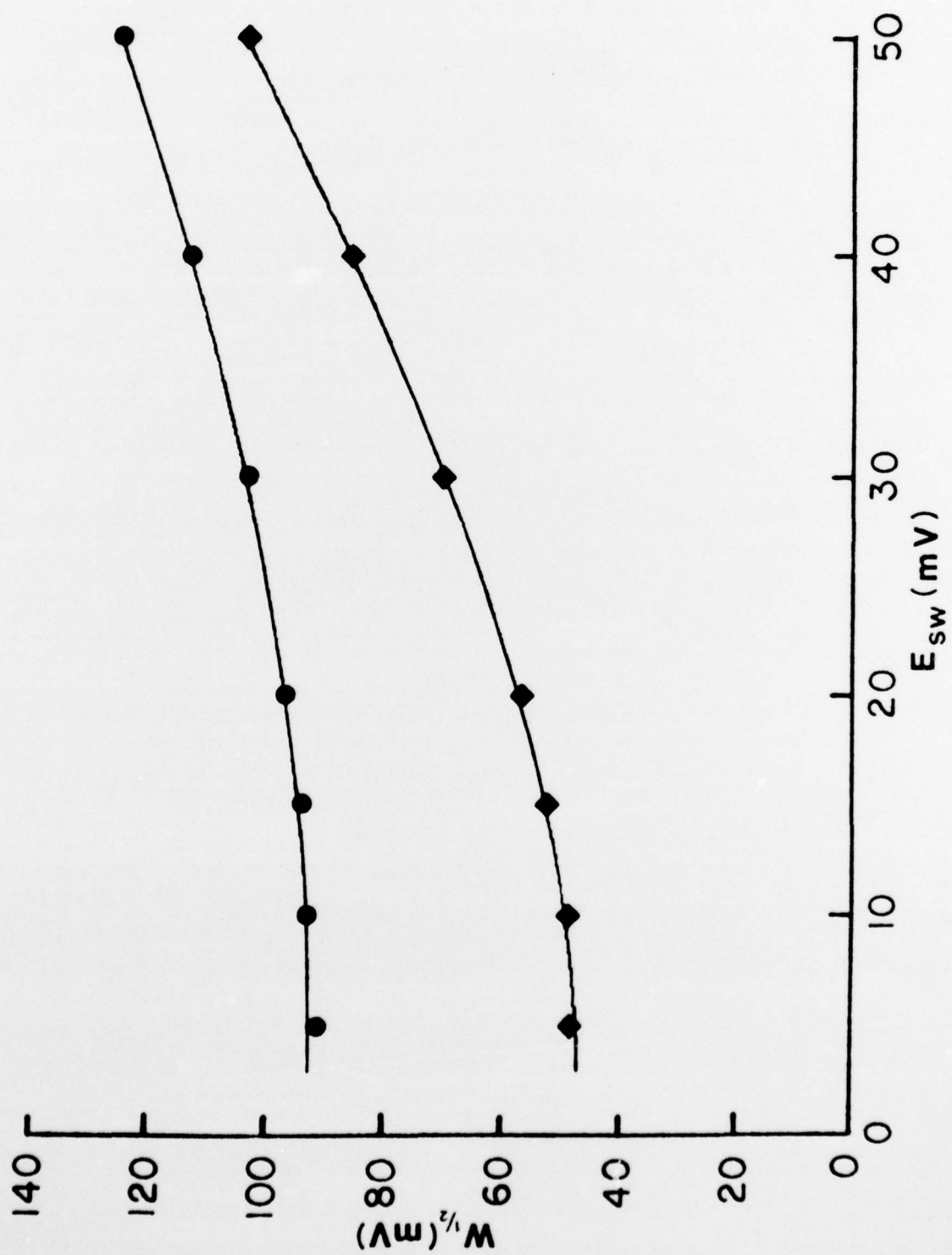


FIGURE 2



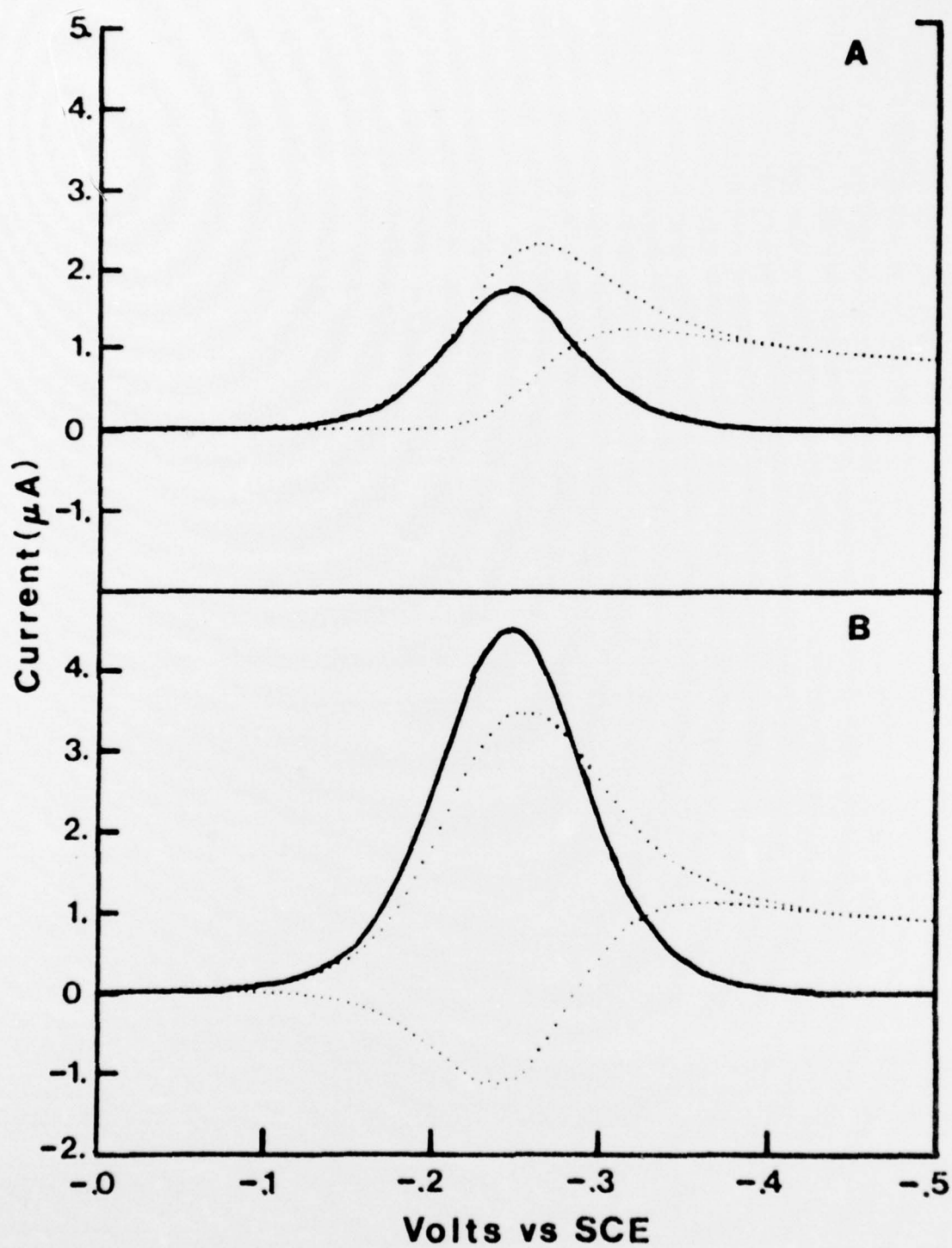


FIGURE 3



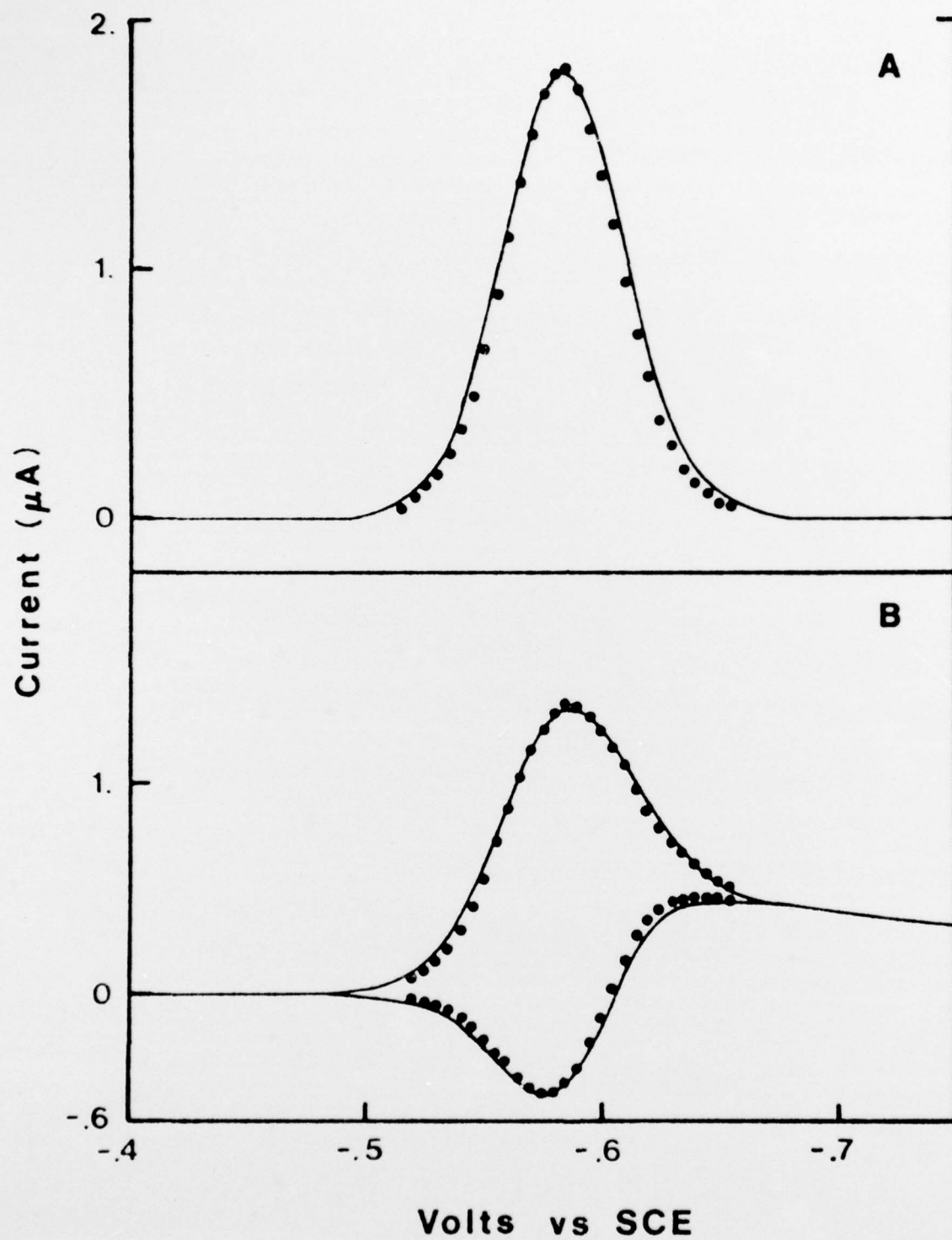


FIGURE 4

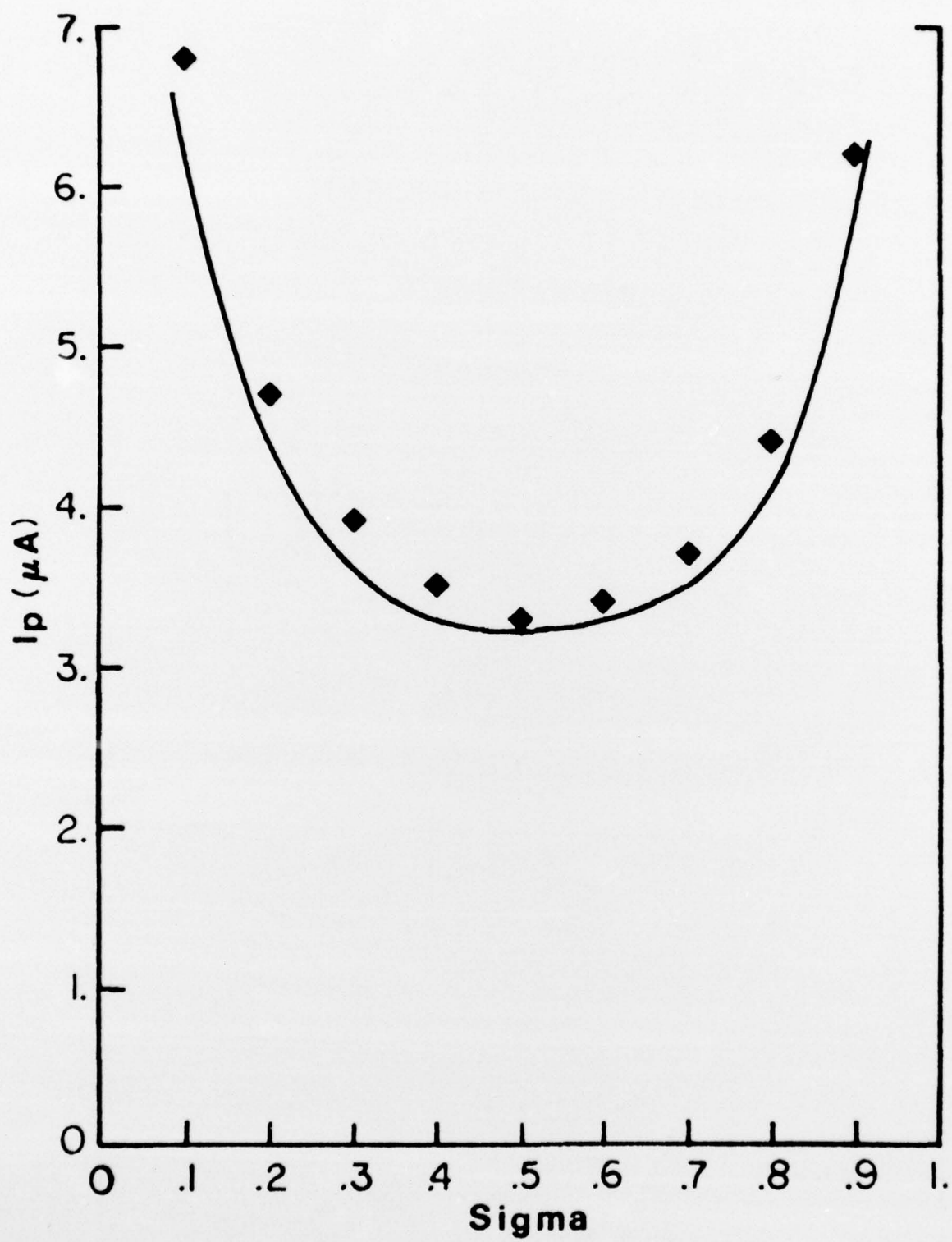


FIGURE 5

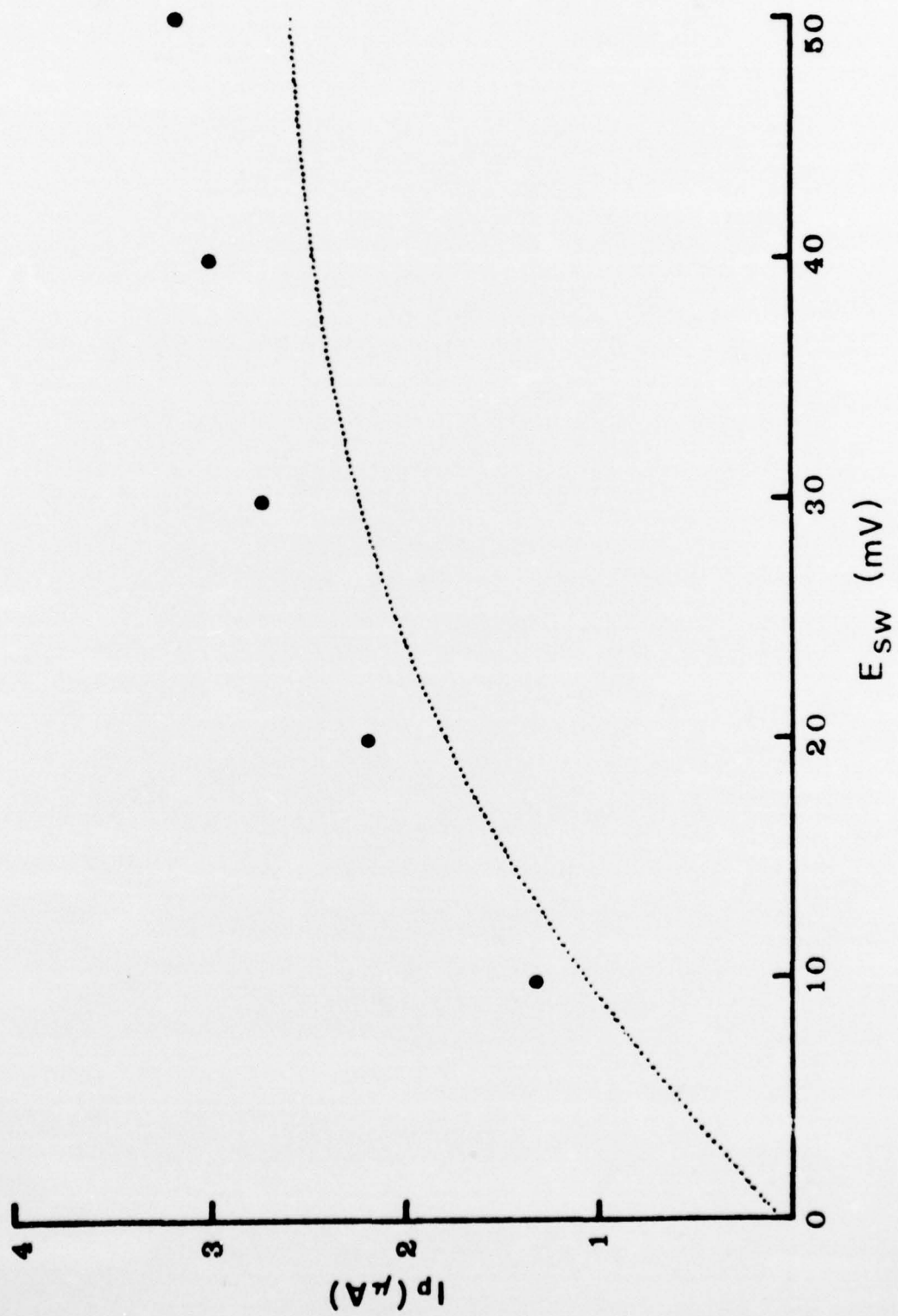


FIGURE 6

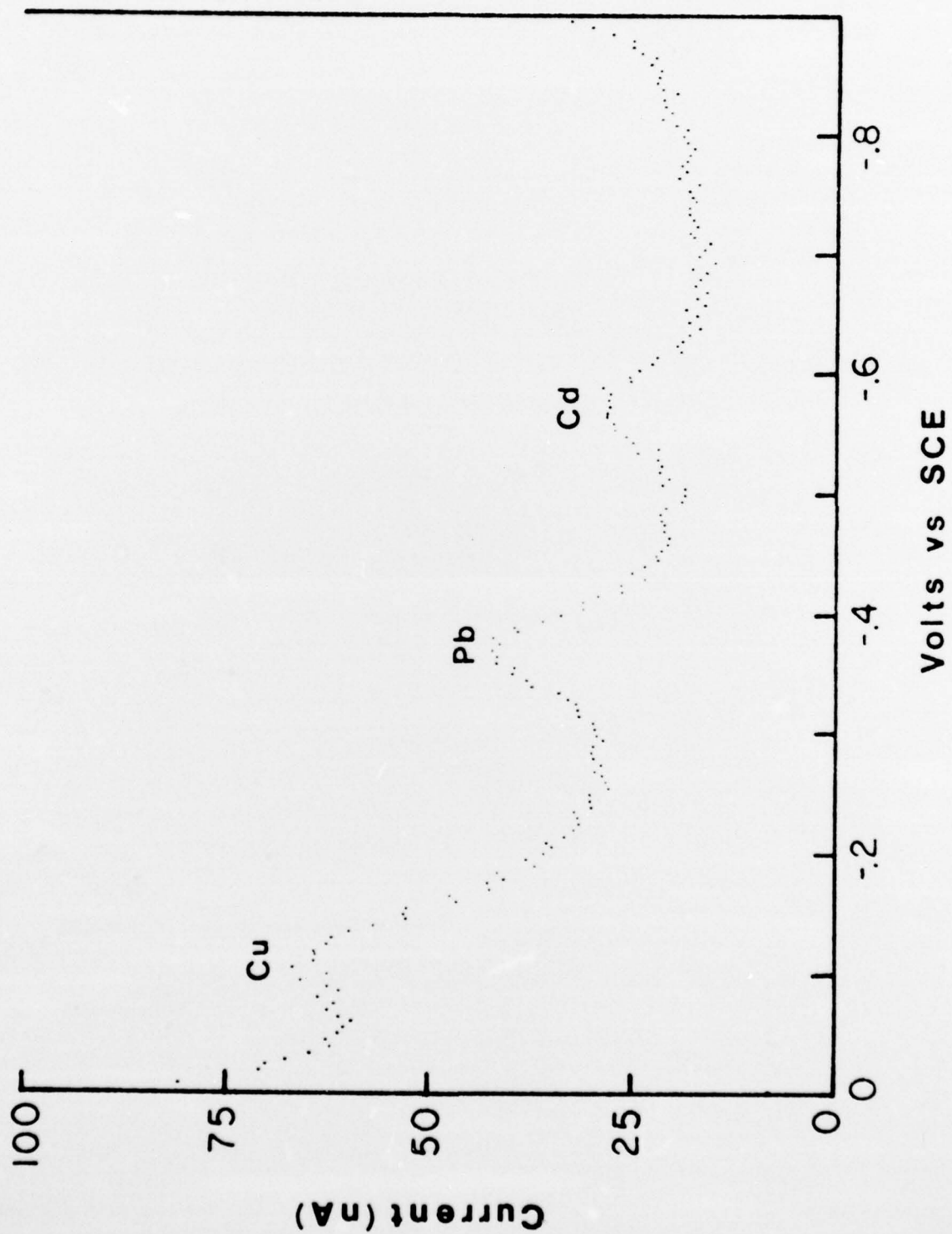


FIGURE 7

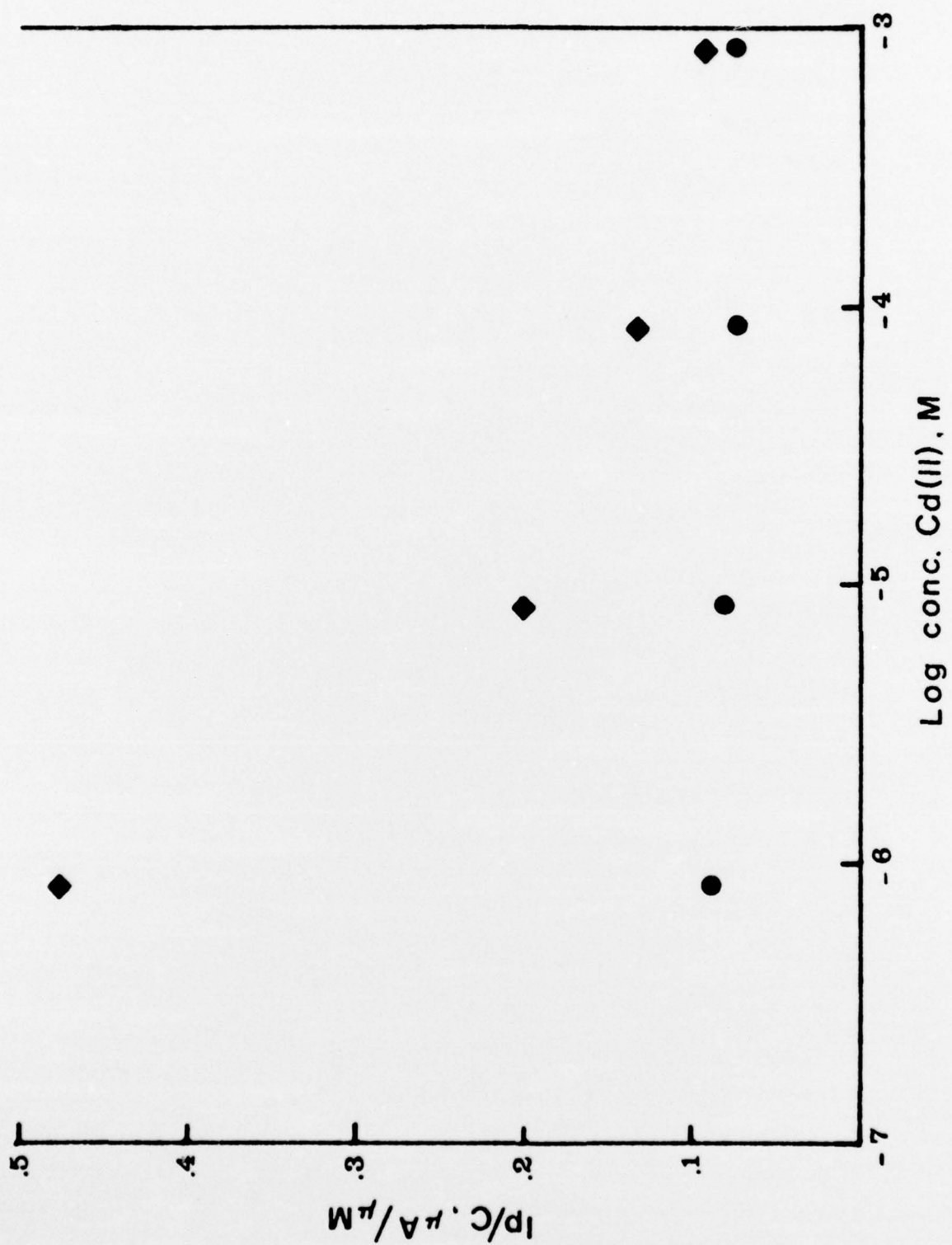


FIGURE 8



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